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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: B01J 23/26, 31/34, C07C 53/124, 53/126, 53/134, 53/136, 57/145, 57/26, 59/01, C07D 207/404, 303/04, 305/04, 309/30, 331/02, C08K 5/01, 5/05, 5/09, 5/10, 5/3412, 5/45, C08L 63/00	A1	(11) International Publication Number: WO 98/56500 (43) International Publication Date: 17 December 1998 (17.12.98)
(21) International Application Number: PCT/US98/12251 (22) International Filing Date: 12 June 1998 (12.06.98) (30) Priority Data: 60/050,078 13 June 1997 (13.06.97) US (71) Applicant (for all designated States except US): DIMENSION TECHNOLOGY CHEMICAL SYSTEMS, INC. [US/US]; 4268 Stencar Drive, Fair Oaks, CA 95628 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): RINDONE, Renato, R. [US/US]; 4268 Stencar Drive, Fair Oaks, CA 95628 (US). MUSKER, W., Kenneth [US/US]; 2437 Evenstar Lane, Davis, CA 95616 (US). (74) Agent: DULIN, Jacques, M.; Heller Ehrman White & McAuliffe, 525 University Avenue, Palo Alto, CA 94301 (US).	(81) Designated States: AU, BG, BR, CA, CN, CZ, EE, FI, GE, HU, ID, IL, JP, KR, LT, LV, MX, NO, PL, RO, SG, SI, SK, TR, UA, US, VN, YU, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	
(54) Title: USE OF CHROMIUM (III) CARBOXYLATES AS A CATALYST (57) Abstract The use of C ₃ -C ₆₀ , substituted or unsubstituted, straight or branch-chained, alkyl, aryl, or aralkyl carboxylate Cr ⁺³ salts, preferably chromium +3 octoate, as catalysts for the reaction of ring systems, such as aziridines, oxiranes, oxetanes and thiiiranes with carboxylic acids, anhydrides, lactone and carbonate esters are disclosed. The use of chromium (Cr ⁺³) salt catalysts for accelerating the reaction of hydroxy compounds with anhydrides, lactones, and carbonate esters are also disclosed. These reactions can occur in single or polymer reactions. The chromium +3 carboxylate catalyst increases the reaction rates by orders of magnitude and selectively reacts the ring systems to form monomers, prepolymers, copolymers, functional end-group monomers, functional end-group prepolymers, and functional end-group polymers rather than forming homopolymers. By varying the catalyst concentration, molar ratios, and reaction temperatures, the reaction time required to form the desired product can be controlled.		

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Title: USE OF CHROMIUM (III) CARBOXYLATES AS A CATALYST

Inventors: RENATO R. RINDONE
W. KENNETH MUSKER

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DESCRIPTION

CROSS REFERENCE TO RELATED APPLICATION:

- 10 This is a Regular application of US Provisional application SN 60/050,078, filed June 13, 1997 for "Use of Chromium (III) Carboxylates as a Catalyst", the benefit of the filing date of which is hereby claimed under 35 USC § 119.

TECHNICAL FIELD:

- 15 This invention relates to the use of known chromium +3 carboxylates as catalysts for reaction of small ring systems, such as aziridines, oxetanes, lactones, carbonate esters, and thiiranes, and for reaction of hydroxy compounds with anhydrides in monomeric or polymeric reactions.

BACKGROUND ART:

- 20 The literature is replete with information showing how to react epoxides with carboxylic acids, anhydrides and imides at room or elevated temperatures. As shown in *Catalysis in Polymer Synthesis*, ACS Symposium Series 496, Edited by E.J. Vandenberg (1992), aluminum porphyrins, mixed with quaternary salts of the type R_4PX and R_4NX , are used to catalyze the reaction of an epoxy with carbon dioxide or anhydrides, but high temperature and/or long reaction times are generally needed. Elastomer
- 25 modified epoxy resins such as diglycidyl ether of bisphenol A (DGEBA) can be made to react with carboxy-terminated polybutadiene-acrylonitrile (CTBN) using triphenyl phosphine, but high reaction temperature or long reaction time is needed to achieve complete reaction. There are a large number of amines, such as polyamide resins like Versamid®, diethylenetriamine, methylenedianiline, that are used to cure various epoxy systems but frequently the cure time is very long and accelerators, such as resorcinol,
- 30 are required. Catalysts, such as the aluminum alkyls (which tend to be very pyrophoric) have been used to promote homo or block polymerization of epoxides, thioepoxides, selenoepoxides and oxetanes. Aziridines have been homopolymerized using a variety of acid catalysts. U.S. Patent No. 3,635,869 (1972) discloses use of chromium +3 carboxylate salts to accelerate the reaction of epoxides with carboxylic acids, anhydrides and imides at room temperature or elevated temperatures.

General references to various catalytic systems include *Epoxy Resin Chemistry II*, ACS Symposium Series 221, Edited by R.S. Bauer (1983). However, such references do not show the use of chromium +3 carboxylates to catalyze ring systems with carboxy-containing compounds, such as carboxylic acids, anhydrides, imides, lactones and carbonate esters.

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THE INVENTION

SUMMARY:

10 It is among the objects and advantages of the invention to employ chromium, Cr^{+3} , catalysts, particularly in the form of carboxylate salts, to catalyze ring systems selectively to block copolymers and end-reactive polymers with controlled molecular weight through the control of catalyst concentration, reaction temperature, and reaction time. It is another object and advantage of the invention to increase by up to several orders of magnitude the reaction rates of the single reaction or the polymerization of ring
15 systems with carboxylic acids, anhydrides, imides, lactones and carbonate esters, and to produce novel prepolymers, polymers, compositions, and compounds, including compounds of pharmaceutical use.

The invention comprises the use of Cr^{+3} salts, e.g., chromium +3 carboxylate salts such as octoates, acetates, butyrates, benzoates, and the like, to enhance or accelerate the reaction of aziridines, oxetanes, thiiranes and oxiranes with carboxylic acids, anhydrides, imides, lactones and
20 carbonate esters to form monomeric or polymeric reaction products. Equally important, chromium +3 carboxylate salts of the invention are used to enhance or accelerate the reaction of hydroxy compounds with anhydrides, lactones, and carbonate esters.

This invention is significant because it discloses the use of chromium +3 carboxylates to promote reactions of small ring systems and hydroxy compounds and finds unique application in the preparation and manufacture of non-polymeric chemicals, new plastic and polymeric materials as well as in improving
25 the reaction or processing conditions of already existing non-polymeric, polymeric and plastic materials. A suitable Cr^{+3} catalyst is HYCAT™ 2000, containing chromium +3 octoate, available from Dimension Technology Chemical Systems, Inc. of Fair Oaks, California.

One advantage of the Cr^{+3} carboxylate catalysts of the invention over existing catalysts is that
30 they do not promote homopolymerization of any of the reactants. The use of Cr^{+3} catalysts results in the synthesis of block copolymers and end-reactive polymers with controlled molecular weight. By adjusting the concentration of the catalyst and reaction temperature, the reaction time can be accurately controlled. Another advantage is that the Cr^{+3} catalysts of the present invention are remarkably universal. Use of a

single Cr^{+3} carboxylate results in copolymerization of the various reactants listed above. In contrast, metalloporphyrin catalysts are not universal; that is, different (e.g., Al, Zn) metalloporphyrins are needed to promote the reaction of different polymeric systems. Furthermore, in the case of the metalloporphyrins, usually a protic cocatalyst compound is needed to promote or initiate the reaction. This is not the case with the Cr^{+3} catalysts of the present invention, in which no additional initiator or cocatalyst is required, although one could optionally be used.

In the chemical reaction systems of the invention, the Cr^{+3} catalysts significantly increase the reaction rates. The overall reaction times are up to several orders of magnitude faster than existing catalyst systems, thereby significantly improving the process economics by providing considerable savings in labor and equipment productivity factors.

DETAILED DESCRIPTION OF THE BEST MODE FOR CARRYING OUT THE INVENTION

The following detailed description illustrates the invention by way of example, not by way of limitation of the principles of the invention. This description will clearly enable one skilled in the art to make and use the invention, and describes several embodiments, adaptations, variations, alternatives and uses of the invention, including what is presently believed to be the best mode of carrying out the invention.

The reactants are identified throughout by chemical nomenclature with reference to typical commercially available sources, by way of example and not by way of limitation. The reactants are also shown in structural format in the equations. It will be recognized by one skilled in the art that the reaction products may be single molecular species, or more complex mixtures of possible reaction products. Thus, while we have shown in the equations the structural formulas of reaction products, those are by way of example and not by way of limitation of the actual or possible products of the process using the Cr^{+3} carboxylate catalysts with the reactants shown in the equation. Accordingly, the invention, without limitation, covers novel products of the inventive catalytic process.

A. Description of the Chromium +3 Carboxylate Catalyst

The catalyst of the present invention is a Cr^{+3} salt. In one embodiment, the Cr^{+3} salt is a $\text{C}_3\text{-C}_{60}$, straight or branch-chained, aryl, alkyl or aralkyl carboxylate. For purposes of this application, an "aryl" group is defined as being derived from an aromatic hydrocarbon typically with 6 to 20 carbon atoms, preferably 6 to 16 carbon atoms, having a single ring (e.g., phenyl), or two or more condensed rings (e.g., naphthyl), or two or more aromatic rings which are linked by a single bond (e.g. biphenyl). The aryl group may optionally be mono-, di- or tri-substituted, independently, with lower branched or straight chain alkyl, lower cycloalkyl with 3 to 12 carbon atoms, lower branched or straight chain alkoxy, lower cycloalkoxy with 3 to 12 carbon atoms, fluoro, chloro, bromo, trifluoromethyl, cyano, nitro and/or difluoromethoxy, and so forth. The Cr^{+3} carboxylate of the invention may optionally be a hexanoate, pentanoate, 2-ethylhexanoate, oleate, stearate, toluate, cresylate, benzoate, alkylbenzoate, alkoxybenzoate, naphthanate, alkoxide, acetate, butyrate, propionate, octoate, and decanoate. In a preferred embodiment, the Cr^{+3} salt is a $\text{C}_3\text{-C}_{10}$, straight or branch-chained, aryl, alkyl or aralkyl carboxylate, such as acetate, butyrate, propionate, benzoate, octoate, and decanoate. In a particularly preferred embodiment of the invention, the catalyst is chromium +3 octoate, where the octoate is a straight or branch-chained C_8 , that may include either, or both, 2-ethyl-hexanoate or octanoate.

The catalyst can be used as a pure compound or may instead be used with a solvent or diluent, such as an alkyl ester of phthalic acid or a high boiling petroleum distillate. Thus the total chromium content in the catalyst employed will range from about 0.5 to the theoretical maximum for the pure carboxylate compound, e.g. about 10.8% for chromium +3 octoate. In a preferred embodiment, the Cr^{+3} concentration in the chromium +3 octoate catalyst is from about 4% to about 8%, by weight. The catalyst/solvent system can range in viscosity from very fluid to very viscous.

The chromium +3 octoate catalyst can be prepared in accordance with Example 1 of U.S. Patent No. 3,968,135, herein incorporated by reference. The preferred chromium +3 octoate concentration in the catalyst is 37.1% to 74.1%, with the balance, 25.9% to 62.9%, being composed of the solvent di-n-heptyl phthalate or a high-boiling petroleum distillate. The solvent in the chromium +3 octoate catalyst is present to aid in the handling of the catalyst, i.e., make it more fluid, dispersible, dispensable and contactible with the reactants in the reaction media and is not an essential component.

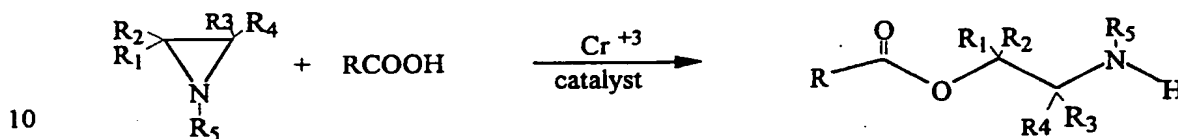
The preferred concentration of chromium in the total reaction media is from about 0.08% to about 2.0%, by weight, and more preferably from about 0.1% to about 0.7%, by weight, based on the combined weight of the reactants.

B. Use of Chromium +3 Carboxylate To Promote Aziridine Reactions

1. The reaction of aziridines with carboxylic acids are accelerated with Cr^{+3} carboxylate catalysts.

(a) Monomeric Systems: Reactions of monofunctional aziridines with monofunctional carboxylic acids.

One embodiment of the present invention is shown in the following equation:



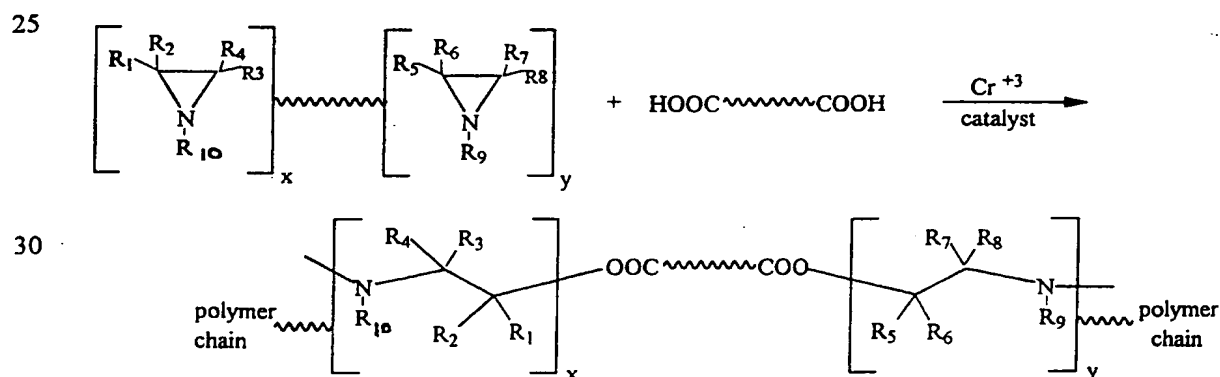
where R_1 through R_5 can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and the monofunctional carboxylic acid can be any molecular weight and composition. The result of the reaction will be ring opening with any carboxylic acid to form single addition product esters with diverse functional groups.

One of ordinary skill in the art will recognize that the specific example, Example 1, provided below, demonstrates that chromium +3 carboxylates can catalyze the reaction between an aziridine and any carboxylic acid, regardless of whether the reactants are monofunctional or polyfunctional.

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(b) Polymeric Systems: Reactions of polyfunctional aziridines with polyfunctional carboxylic acids.

Another embodiment of the present invention is shown in the following equation:



where R_1 through R_{10} can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and the polyfunctional carboxylic acid can be any molecular weight and composition provided that it contains at a minimum at least an average of 1.0 equivalents of the carboxylic acid group per mole and the aziridine combination, x and y are each at least 1, denoting a polyfunctional aziridine compound. The result of the reaction will be ring opening to form polyamine-esters containing diverse functional groups.

The following specific example illustrates one embodiment of chromium +3 catalysis of the reaction of an aziridine with a polyfunctional carboxylic acid:

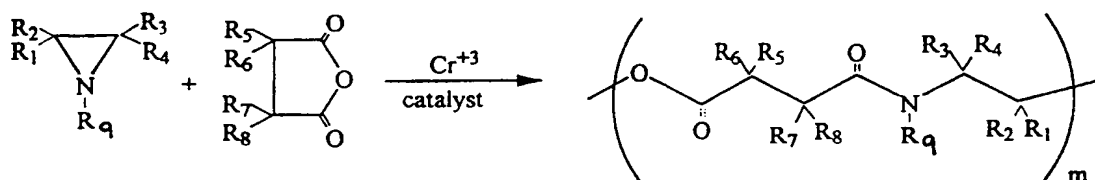
Example 1. Reaction of pentaerythritol-tris-B-(N-aziridinyl)-propionate with a dimer acid.

Into a mixing cup (Paul N. Garner, 95 mm diameter x 47 mm deep) was weighed 15.5 grams (100.3 meq) of pentaerythritol-tris-B-(N-aziridinyl)-propionate (commercially available as Xama-7™ from EIT, Inc.), 27.7 grams (101.6 meq) of a dimer acid (commercially available as Empol® 1016 dimer acid from Henkel Corporation), and 4.28 grams (0.5% Cr^{+3} based on the weight of the reactants) of the Cr^{+3} of the invention and mixed for 2 minutes with a spatula, then placed in a Garner wire-stirred standard gel timer (Model GT-S) at 32 °C. After 1 minute of stirring, the contents of the cup were completely solidified into a hard rubbery mass.

As a control, the identical reaction was also performed without the use of the chromium catalyst. Into an aluminum weighing dish (Whatman No. 8283, 60 mm diameter x 13 mm deep) was weighed 1.6 grams (10.36 meq) of pentaerythritol-tris-B-(N-aziridinyl)-propionate and 2.7 grams (9.90 meq) of dimer acid and mixed for 2 minutes with a spatula, then allowed to stand at 32 °C overnight. The composition was tacky after 15 minutes and solidified into a semi-tacky mass in about 24 hours.

2. The reaction of aziridines with anhydrides is accelerated with the Cr^{+3} carboxylate catalyst.

One embodiment of the present invention is shown in the following equation:



where R_1 through R_9 can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and m is at

least 1. The result of the reaction will be the ring opening of the aziridine with an anhydride, thereby forming an ester-amide polymer.

The following specific example illustrates one embodiment of these reactions of aziridines with anhydrides in the presence of the Cr^{+3} carboxylate catalyst:

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Example 2. Reaction of pentaerythritol-tris-B-(N-aziridinyl)-propionate with methyl hexahydrophthalic anhydride (MHHPA).

MHHPA, 4.3g (51.1 meq) and pentaerythritol-tris-B-(N-aziridinyl)-propionate (identified in Example 1, above), 2.5g (17.6 meq) were weighed into a 30 ml beaker and thoroughly mixed. A small sample, 0.6g, was transferred into a 15 ml beaker for a control. To the larger portion, 6.2g, was added 0.2g (0.26% Cr based on the weight of the reactants) of the Cr^{+3} catalyst. The contents of both flasks were allowed to react at room temperature, 22 °C. After a 10 minute reaction period the chromium catalyzed material was no longer mobile when the beaker was tipped on its side. The material in the control beaker was still mobile. After a 25 minute reaction period the control reaction was not mobile. Although the chromium catalyzed reaction was complete at least twice as fast as the control reaction, both the control and chromium catalyzed reaction products showed an equal amount of hardness when prodded with a pointed spatula. Both reaction products were insoluble in acetone.

Example 3. Reaction of pentaerythritol-tris-B-(N-aziridinyl)-propionate with bicyclo (2.2.2) oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA).

Into an aluminum weighing pan was put 6.6g (53.2 meq) of BTA, 7.7g (54.1 meq) of pentaerythritol-tris-B-(N-aziridinyl)-propionate (identified in Example 1, above) and 0.4g of the Cr^{+3} catalyst (0.1 wt % chromium based on the weight of the reactants). After 45 minutes at 41°C the contents of the pan cured to a hard, brittle olive green solid.

It will be evident to one of ordinary skill in the art that Example 2 and 2b, above, also provides evidence that the Cr^{+3} catalyst of the invention can be used to accelerate the reaction of polyfunctional aziridines and/or anhydrides, as well as that of monofunctional reactants.

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3. Aziridines are not homopolymerized by the Cr^{+3} carboxylate catalyst.

The following specific example demonstrates that the Cr^{+3} carboxylate catalyst of the invention does not promote the homopolymerization of aziridines:

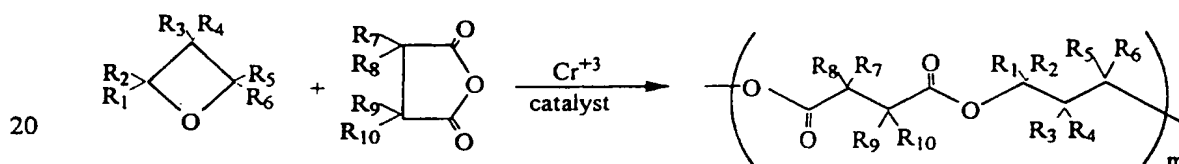
Example 4. Attempted homopolymerization of pentaerythritol-tris-B-(N-aziridinyl)-propionate with Cr^{+3} catalyst.

To show that pentaerythritol-tris-B-(N-aziridinyl)-propionate (identified in Example 1, above) does not homopolymerize in the presence of Cr^{+3} catalyst at elevated temperature, 6.8 grams of pentaerythritol-tris-B-(N-aziridinyl)-propionate and 0.4 g of the Cr^{+3} catalyst (0.3% chromium based on the weight of pentaerythritol-tris-B-(N-aziridinyl)-propionate) was placed into an aluminum weighting pan and heated to 41°C for 3 hours and 15 minutes then allowed to stand at 16 to 21°C for 9 days at which time the contents of the pan was still liquid.

C. Use of Chromium $+3$ Carboxylate to Promote Oxetane Reactions

1. The reaction of oxetanes with anhydrides is accelerated with Cr^{+3} carboxylate catalysts.

In one embodiment, the present invention provides for the following reaction:



where R_1 through R_{10} can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and m is at least 1. The result of the reaction will be polyesters with or without pendant hydroxyl or carboxylic acid groups depending on the mole ratio of the oxetane to anhydride employed.

The following specific example illustrates one embodiment of Cr^{+3} catalysis of the reaction of oxetanes with anhydrides.

Example 5. Reaction of 3-bromomethyl, 3-methyloxetane (BMMO) with methyl hexahydrophthalic anhydride (MHHPA).

MHHPA, 2.6g (15.5 mmol) and BMMO, 2.5g (15.1 mmol, 3% excess) were weighed into a 50 ml Erlenmeyer flask and thoroughly mixed. A small sample, 1.0g was transferred into a 25 ml Erlenmeyer flask for a control. To the larger portion, 4.1g, was added 0.3g (0.6% Cr based on the weight of the reactants) of the Cr^{+3} catalyst. The contents of both flasks were simultaneously

heated to 95 to 100 °C in a hot oil bath for a period of 1½ hours. Samples were periodically taken from each flask for FTIR analysis. After a 30 minute reaction period, a new, very strong ester carbonyl peak was observed in the chromium catalyzed reaction at 1734 cm⁻¹ along with the anhydride carbonyl peaks at 1861 cm⁻¹ and 1787 cm⁻¹. Because the chromium catalyzed material would immediately solidify when removed from the reaction flask, additional samples could not be taken for FTIR analysis. On completion of the reaction, when the chromium catalyzed reaction product was cooled to room temperature, a hard polymer formed. Conversely, the control samples remained liquid though out the reaction period and upon cooling to room temperature. FTIR analysis of the control material showed no apparent change in chemical composition during the heating period. Titration with sodium hydroxide of a sample of the chromium catalyzed reaction mixture showed this material contained 2.58 mmol of unreacted MHHPA. The amount of MHHPA that was converted to product in the chromium catalyzed reaction was 81.9%.

It will be evident to one of ordinary skill in the art that Example 5, above, demonstrates that the Cr⁺³ catalyst of the invention can also be used to accelerate the reactions of both monofunctional and polyfunctional oxetanes and anhydrides.

2. Importance of the Cr⁺³ carboxylate catalyst in the reaction of oxetanes with anhydrides: a comparison with other metal carboxylate catalysts.

To show the importance of using the Cr⁺³ carboxylate catalysts, other metal carboxylates, such as cobalt octoate and nickel octoate, were used in an attempt to accelerate the oxetane reaction with an anhydride. Neither cobalt nor nickel carboxylates were found to be useful in promoting these reactions.

Example 6. Attempted reaction of methyl hexahydrophthalic anhydride (MHHPA) with 3-bromomethyl-3-methyl-oxetane (BMMO) catalyzed by the cobalt salt of 2-ethylhexanoic acid.

MHHPA, 3.4g (20.2 mmol) and BMMO 3.3g (20.0 mmol) were weighed into a 50 ml Erlenmeyer flask and 0.55g, (0.5% Co based on the weight of the reactants) of the cobalt octoate catalyst was added and thoroughly mixed. The flask was heated to 100 ± 2 °C in a hot oil bath for a period of two hours and 10 minutes. Samples were periodically taken from the flask for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the anhydride carbonyl groups (1861 and 1787 cm⁻¹) converting to an ester carbonyl at 1731 cm⁻¹. Only a slight

ester carbonyl absorption at 1731 cm^{-1} was detected at the end of the reaction. These data show that Co^{+3} , in the presence of the 2-ethylhexanoate anion, does not accelerate the reaction of BMMO with MHPA.

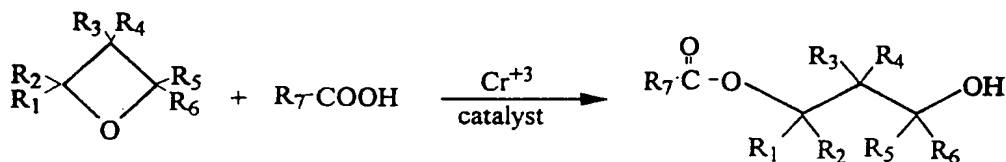
5 **Example 7.** Attempted reaction of methyl hexahydro phthalic anhydride (MHPA) with 3-bromomethyl-3-methyl-oxetane (BMMO) catalyzed by the nickel salt of 2-ethylhexanoic acid.

MHPA, 3.4g (20.2 mmol) and BMMO 3.4g (20.6 mmol) were weighed into a 50 ml Erlenmeyer flask and 0.45g, (0.5% Ni based on the weight of the reactants) of the nickel octoate catalyst was added and thoroughly mixed. The flask was heated to $100 \pm 2^\circ\text{C}$ in a hot oil bath for a period of 1.75 hours. Samples were periodically taken from the flask for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the anhydride carbonyl groups (1861 and 1787 cm^{-1}) converting to an ester carbonyl at 1731 cm^{-1} . A gelatinous material formed during the reaction, which liquefied on standing at room temperature for 24 hours. Only a slight ester carbonyl absorption at 1731 cm^{-1} was detected at the end of the reaction. Based on the titration of the reaction product, nearly all, 99.4%, of the MHPA was recovered. These data show that Ni^{+2} , in the presence of the 2-ethyl hexanoate anion, does not accelerate the reaction of BMMO with MHPA.

3. The reaction of oxetanes with carboxylic acids is accelerated with Cr^{+3} carboxylate catalysts.

(a) Monomeric Systems: Reactions of oxetanes with monofunctional carboxylic acids.

25 One embodiment of the invention is shown by the following equation:



30 where R through R₇ can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups. The products of the reaction are gamma-terminated hydroxy esters.

The following specific examples illustrates one embodiment of the reaction of oxetanes with monofunctional carboxylic acids:

Example 8. Reaction of 3-bromomethyl, 3-methyl-oxetane (BMMO) with 2-ethylhexanoic acid.

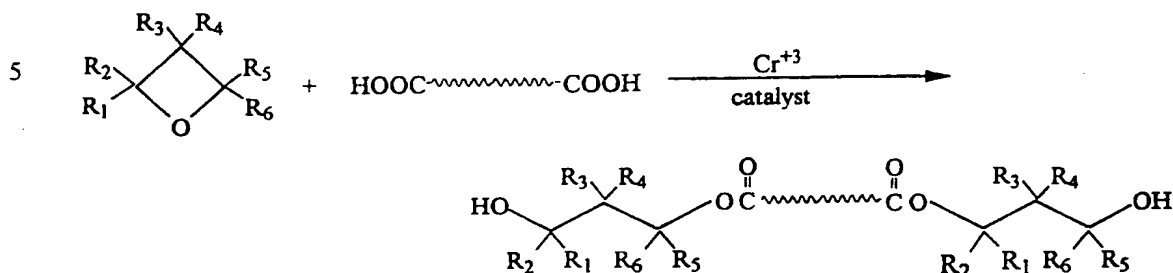
5 BMMO, 3.3g (20.0 mmol) and 2-ethylhexanoic acid, 2.9g (20.1 mmol) were weighed into a 50 ml Erlenmeyer flask and a 0.8 g portion was transferred into a 25 ml Erlenmeyer flask to serve as a control. To the major portion, 5.4g, was added 0.3g (0.4% Cr based on the weight of the reactants) of the Cr^{+3} catalyst and thoroughly mixed. Both flasks were heated to 74 to 77° C in a hot oil bath for a period of 5 hours and 20 minutes. Samples were periodically taken from both
10 flasks for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the acid carbonyl (1701 cm^{-1}) converting to an ester carbonyl (1735 cm^{-1}) and the formation of a hydroxyl group (3450 cm^{-1}) due to opening of the oxetane ring as the reaction proceeded. The relative reaction rate was determined by following the ratio of the ester carbonyl absorption peak to the acid carbonyl absorption peak in the control and the chromium catalyzed reactions. In the
15 control reaction the ratio of the ester carbonyl to the acid carbonyl increased from 0.57:1.0 to 0.70:1.0, respectively, in 320 minutes. In the chromium catalyzed reaction the ratio of the ester carbonyl to the acid carbonyl increased from 0.60:1.0 to 1.27:1.0 in 315 minutes. Comparatively, the chromium catalyzed reaction was 73 times faster than the control reaction. The amount of unreacted 2-ethylhexanoic acid was determined (5.66 mmol) in the chromium catalyzed reaction
20 product by titration with 0.0974 N sodium hydroxide and showed an overall conversion of 68.4%.

Example 9. Reaction of 3-bromomethyl 3-methyl-oxetane (BMMO) with benzoic acid.

BMMO, 3.5g (21.2 mmol) and benzoic acid, 2.4g (19.7 mmol) were weighed into a 50 ml Erlenmeyer flask and 2.0g, (2.7% Cr based on the weight of the reactants) of the Cr^{+3} catalyst was
25 added and thoroughly mixed. The flask was heated to 97 to 100 °C in a hot oil bath for a period of 4 hours. Samples were periodically taken from the flask for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the acid carbonyl (1700 cm^{-1}) converting to an ester carbonyl (1723 cm^{-1}) and the formation of a hydroxyl group (3447 cm^{-1}) due to opening of the oxetane ring as the reaction proceeded. The reaction was considered complete when the acid
30 carbonyl absorption peak could no longer be seen. The amount of unreacted benzoic acid was determined (5.3 mmol) by titration with 0.0974 N sodium hydroxide and showed an overall conversion of 84.6%.

(b) Polymeric systems: Reactions of oxetanes with polyfunctional carboxylic acids.

Another embodiment of the invention is shown by the following equation:



where R₁ through R₆ can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups. The products of the reaction are polymeric esters with pendent hydroxyl groups.

The following specific examples illustrate one embodiment of the Cr⁺³-catalyzed reaction of oxetanes with polyfunctional carboxylic acids:

15

Example 10. Reaction of 3-bromomethyl-3-methyloxetane (BMMO) with a dimer acid.

4.8g (8 mmol) of the dimer acid used in Example 1, 2.9g (17.6 mmol, 10% excess) of BMMO and 1.1 g (1.1% Cr based on the weight of the reactants) of the Cr⁺³ catalyst were weighed into a 50 ml Erlenmeyer flask and the solution heated to 96 to 98 °C in a hot oil bath for a period of 6 1/3 hours. Samples were periodically taken for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the acid carbonyl (1710 cm⁻¹) converting to an ester carbonyl (1738 cm⁻¹) and the formation of a hydroxyl group (3444 cm⁻¹) due to opening of the oxetane ring as the reaction proceeded. After one hour, the absorption of the acid carbonyl was very slight and appeared as a shoulder on the ester carbonyl peak and could not be measured and the hydroxyl absorption was at its maximum. Both of these observations showed the reaction was complete. The reaction was heated for an additional 5 1/3 hours to see if any additional changes could be seen in the carbonyl region of the FTIR spectra. None were observed, indicating that the reaction had proceeded to completion within the first hour.

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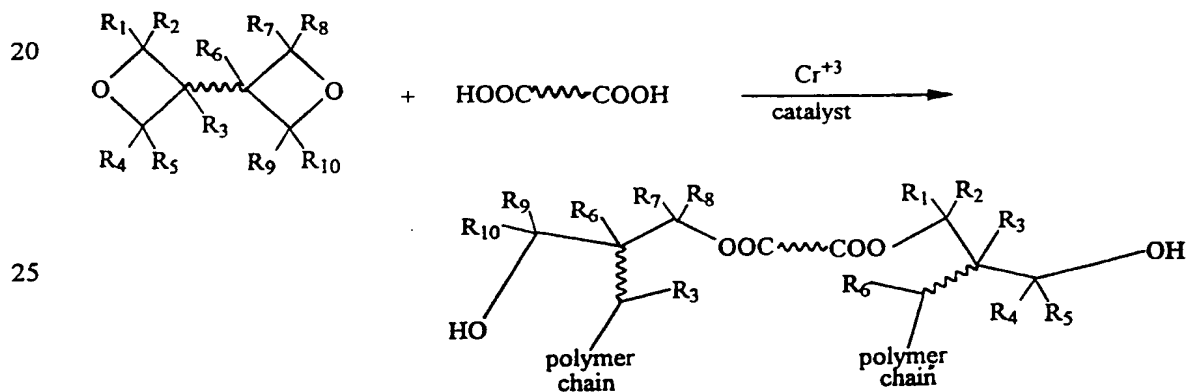
Example 11. Reaction of 3-bromomethyl-3-methyloxetane (BMMO) with dimer acid.

2.8g (4.7 mmol) of the dimer acid identified in Example 1, above, and 1.6g (9.7 mmol, 3% excess) of BMMO were weighed into a 50 ml Erlenmeyer flask and thoroughly mixed. A small sample, 0.8 g was transferred into a 25 ml Erlenmeyer flask for a control. To the larger portion was

added 0.4g (0.9% Cr based on the weight of the reactants) of the Cr^{+3} catalyst. The contents of both flasks were simultaneously heated to 95 to 106 °C in a hot oil bath for a period of 5 hours. Samples were periodically taken for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the acid carbonyl (1710 cm^{-1}) converting to an ester carbonyl (1738 cm^{-1}) and the formation of a hydroxyl group (3444 cm^{-1}) due to opening of the oxetane ring as the reaction proceeded. After 5 hours, analysis of the control sample showed that no hydroxyl group was formed and the ester carbonyl absorption peak was only a slight blip (that could not be measured) on the shoulder of the acid carbonyl absorption peak. However, the sample with the chromium catalyst showed the reaction was complete after 2½ hours of reaction. Both of these observations showed that the Cr^{+3} carboxylate catalyzed the reaction of the oxetane with the carboxylic acid, as compared to the uncatalyzed reaction.

(c) **Polymeric systems: Reaction of polyfunctional oxetanes with carboxylic acids.**

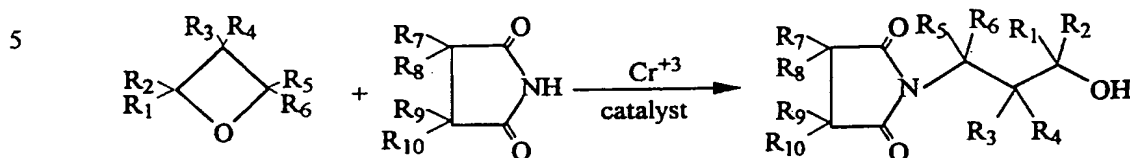
Based on the evidence given in Examples 8, 9, 10, and 11, above, it will be evident to one of ordinary skill in the art that the reaction of di- or poly-functional oxetanes with di- or polyfunctional carboxylic acids will produce new and useful polymers with pendent hydroxy or carboxylic groups depending on the mole ratio of the oxetanes and carboxylic acids employed. Accordingly, the present invention also provides for the reaction shown in the following equation.



where R_1 through R_{10} can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and the polyfunctional carboxylic acid can be any molecular weight and composition provided that it contains at a minimum at least an average of 1.0 equivalent of carboxylic acid group per mole. The result of the reaction are polyesters, polyols, and/or carboxylic acids.

4. The reaction of oxetanes with imides is accelerated with Cr^{+3} carboxylate catalysts.

Another example of the catalyst of the invention is illustrated in the following reaction:



where R_1 through R_{10} can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups. One of ordinary skill in the art will readily recognize that the result of the reaction will be a gamma-hydroxy terminated imide.

Example 12. Reaction of 3-bromomethyl-3-methyloxetane (BMMO) with succinimide

15 Succinimide, 2.9g (29.3 mmol) and BMMO, 4.7g (28.5 mmol) and 10 ml of 2-methyltetrahydrofuran (solvent) and 0.8g (0.8 % Cr based on the weight of the reactants) of the activated Cr^{+3} catalyst was put into a 50 ml Erlenmeyer flask and thoroughly mixed. The slurry was heated to 65 to 70°C in a hot oil bath for a period of 1 hour and 55 minutes. Samples were periodically taken from the flask for FTIR analysis. After 10 minutes about 50 % of the solids were dissolved; after 50 minutes about 90 % of the solids were dissolved and after 1 hour and 45 minutes all of the solids were dissolved. During this time a new, very strong carbonyl peak was observed being formed at 1709 cm^{-1} and the appearance of a hydroxyl group was also observed at 3461 cm^{-1} .

20 The reaction mixture was allowed to cool to room temperature and about 0.3 grams of solids were removed by filtration and air dried (mp 115 to 122°C; succinimide mp: 123-125°C). The filtrate was concentrated *in vacuo* first at water aspirator vacuum at 72°C then at vacuum pump pressure and 65 to 70°C. The weight of the concentrate was 6.9 grams. The concentrate was loaded onto a chromatography column (5 inch long by 1/2 inch diameter) containing chromatography grade alumina and then eluted first with 40 ml of methylene chloride followed by 50 ml of methanol. Both eluents were concentrated in *vacuo* as before. The methylene chloride eluent concentrate was a liquid and weighed 4.8 grams (64% yield). The methanol eluent concentrate, 1.5 grams (20 % crude yield) was a pasty solid but had an IR spectra very similar to the product recovered from the methylene chloride eluent concentrate.

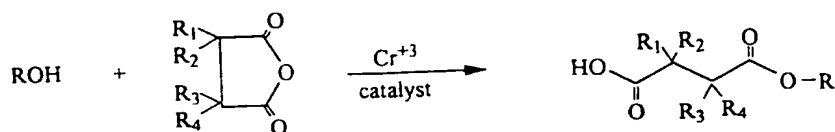
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It will be evident to one of ordinary skill in the art that Example 12, above, demonstrates that the Cr^{-3} catalyst of the invention can not only be used to accelerate the reactions of monofunctional oxetanes and imides, but of polyfunctional oxetanes and imides as well.

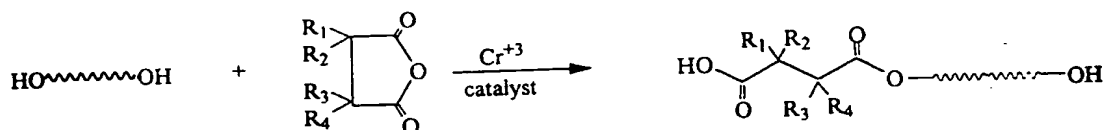
5 D. Use Of Chromium +3 Carboxylate To Promote Hydroxy Compound Reactions

1. The reaction of hydroxy compounds with anhydrides is accelerated with Cr^{+3} carboxylate catalysts.

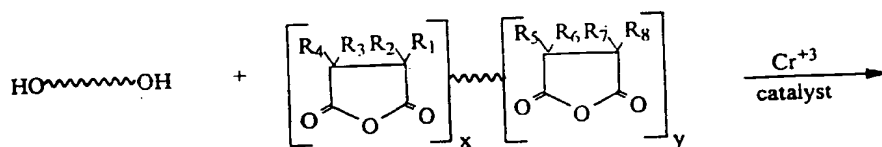
10 This embodiment of the invention is shown in the following equations.



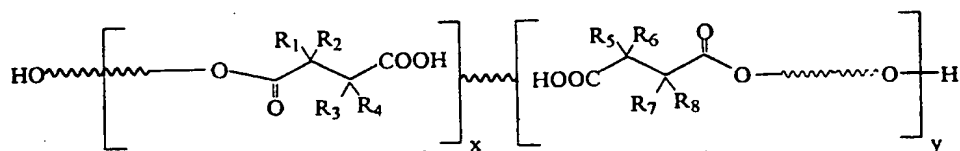
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where R through R_8 can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and where x and y are each at least 1, denoting a polyfunctional anhydride compound of any composition and molecular weight and the hydroxyl group can be in the form of a mono to polyfunctional hydroxy compound of any

composition and molecular weight. The products of the reaction are either non-polymeric or polymeric esters with pendent hydroxyl or carboxylic acid groups depending on the mole ratio of the reactants.

The following specific examples illustrate the ability of Cr^{+3} carboxylate to promote hydroxy compound reactions under different conditions:

5

Example 13. Reaction of methyl hexahydrophthalic anhydride (MHHPA) with a dihydroxy ester resin.

MHHPA, 33.6g (199.8 mmol), a dihydroxy ester resin (commercially available as Formrez[®] 11-112 from Witco Corp.), 100.6g (200.0 meq) and 8.5g of the Cr^{+3} catalyst (0.5 wt % chromium based on the weight of the reactants) were weighed into a 250 ml Erlenmeyer flask and thoroughly mixed. The sample was heated to $75 \pm 3^\circ\text{C}$ in a water bath for 6 hours and 10 minutes. Samples were periodically taken for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the anhydride carbonyl groups (1788 cm^{-1} and 1857 cm^{-1}) converting to an ester carbonyl group (1734 cm^{-1}). The intensity of these peaks were compared to an absorption peak, at 1454 cm^{-1} that appeared to remain constant throughout the reaction. After 4 hours the anhydride carbonyl absorption peak (1788 cm^{-1}) was only a slight blip on the shoulder of the ester carbonyl absorption peak. Two hours later, no anhydride carbonyl peak absorption could be detected. The ratio of the "constant" peak to the anhydride peak (1788 cm^{-1}) increased from 0.44:1.0 to >128:1.0, respectively, in 250 minutes. In a control run, where no chromium catalyst was used, 10.2g (20.3 mmol) of the dihydroxy ester resin and 3.5g (20.8 mmol) MHHPA were reacted at 74 to 85°C . Even though the control run was conducted at a higher average reaction temperature than the experiment containing the chromium catalyst, the rate of increase of the "constant" peak to the anhydride peak was significantly lower, going from 0.44:1.0 to 0.93:1.0, respectively, in 263 minutes. Comparatively, the chromium catalyzed reaction was 138 times faster than the control run. A sample, 0.6625g, of the reaction product in the chromium-catalyzed reaction was titrated to the end point with 9.76 ml (950.6 mmol) 0.0974 N sodium hydroxide. Based on this titration, the total acid content in the reaction product is 204.7 mmol. This corresponds to a 98.8% conversion of the MHHPA to the product. These observations showed that the Cr^{+3} catalyst accelerated the reaction of the anhydride with the difunctional hydroxy compound.

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Example 14. Reaction of methyl hexahydrophthalic anhydride (MHHPA) with a dihydroxy ester resin.

3.4g (20.2 mmol) of MHHPA and, 10.2g (10.1 mmol) of the dihydroxy ester resin identified in Example 13, above, were weighed into a 50 ml Erlenmeyer flask and 1.2g, (0.7% Cr based on the

weight of the reactants) of the Cr^{+3} catalyst was added and thoroughly mixed. The flask was heated to $99 \pm 1^\circ\text{C}$ in a hot oil bath for a period of 2.5 hours. Samples were periodically taken from the flask for FTIR analysis. The reaction was followed by observing the change in the absorption ratio of the anhydride carbonyl groups (1857 and 1788 cm^{-1}) converting to an ester carbonyl (1734 cm^{-1}).

- 5 The reaction was considered complete when the anhydride carbonyl absorption peak was just a small shoulder on the ester peak. The reaction product was titrated with 0.0974 N sodium hydroxide and showed an overall conversion of 93.9% .

10 **Example 15.** Reaction of a copolymer of maleic anhydride and styrene with a dihydroxy ester resin.

Into an aluminum weighing pan was placed 3.7g (26.7 mmol anhydride) of a copolymer of maleic anhydride and styrene (commercially available as Scripset® 520 from Monsanto Company), 6.6g (13.1 meq) of the dihydroxy ester (used and identified in Example 13) and 0.3g (0.15% Cr based on the weight of the reactants) of the Cr^{+3} catalyst and heated to 54 to 60°C for a period of 5
15 hours during which time a flexible polymer was formed. The pan was heated for an additional 12.5 hours at 54°C but no change in the consistency of the very elastic polymer was observed. After storing the polymer at room temperature for 10 months no change in the polymer appearance, including no shrinkage, was observed.

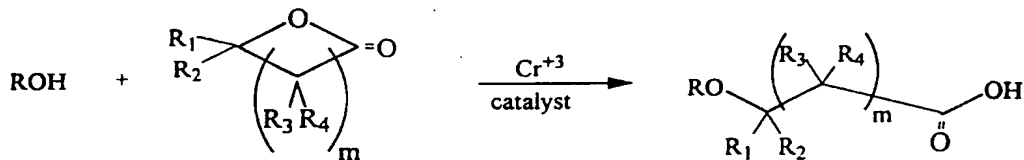
In a separate control run without using the chromium catalyst, 2.5g (18.1 mmol anhydride)
20 of the maleic anhydride/styrene copolymer was mixed with 4.6g (9.1 meq) dihydroxy ester and heated to 57°C for 20 hours. After $1\frac{1}{4}$ hours a gel started to form that was very sticky and not elastic in comparison to the polymer made with the chromium catalyst. After 20 hours the reactants were completely polymerized but the polymer remained very sticky. After storage at room temperature for 10 months the polymer remained sticky and there appeared to be some shrinkage.

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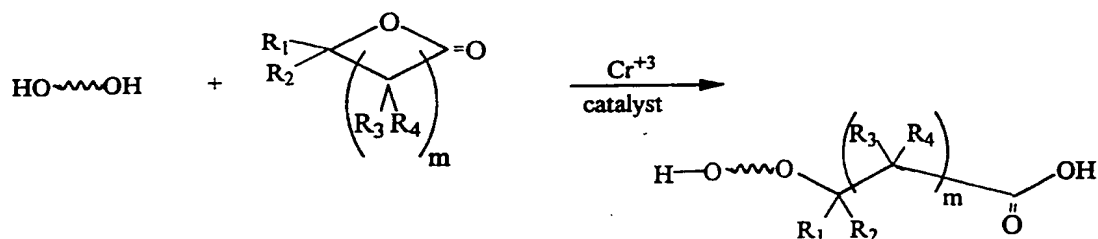
2. The reaction of hydroxy compounds with lactones is accelerated with Cr^{+3} carboxylate catalysts.

Another embodiment of the present invention is shown in the following equations:

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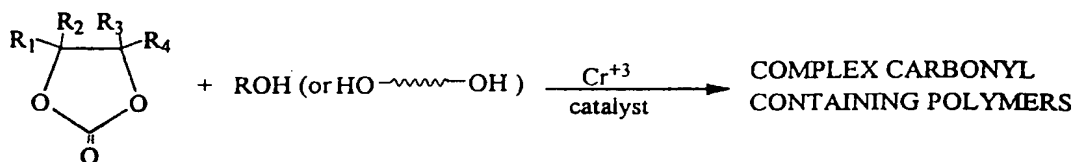


10 where R through R₄ can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and the hydroxy compound can be any molecular weight and composition provided that it contains at a minimum at least an average of 1.0 equivalents of hydroxyl group per mole and m is at least 1, representing at least one carbon in the lactone ring. The result will be reaction of lactones with single or polyhydroxy compounds forming monomer or poly-ether-esters.

15 Based on the evidence given in Examples 13, 14, and 15. above. and Example 16, below, it appears that Cr⁺³ carboxylate will accelerate the reaction of lactones with hydroxy compounds.

3. The reactions of hydroxy compounds with carbonate esters is accelerated with Cr⁺³ carboxylate catalysts.

Another embodiment of the present invention is shown in the following equation:



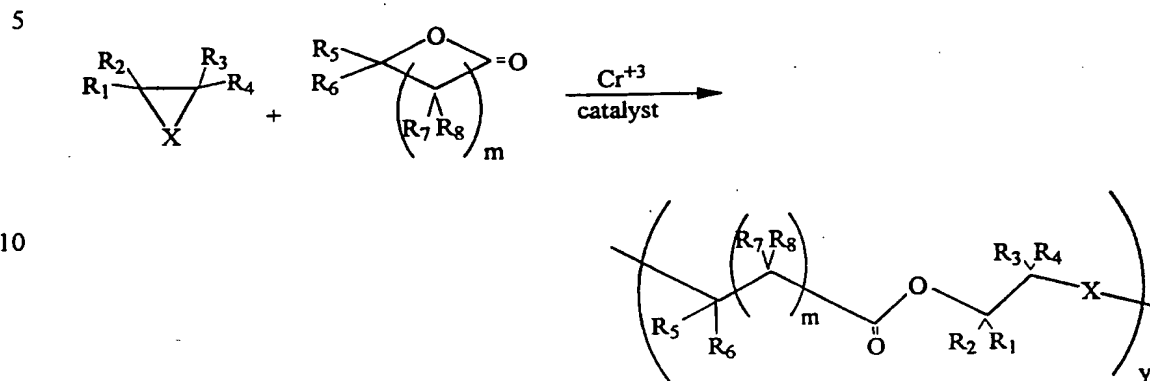
25 where R through R₄ can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and the hydroxy compound can be any molecular weight and composition provided that it contains at a minimum at least an average of 1.0 equivalents of hydroxyl group per mole. The result of the reaction will be a complex monomer or polymer ether ester.

30 Based on the evidence given in Examples 13, 14 and 15. above. and Example 17, below, it appears that Cr⁺³ carboxylate will accelerate the reaction of carbonate esters with hydroxy compounds.

E. The Use Of Chromium +3 Carboxylate To Promote Other Ring Reactions

1. Cr^{+3} carboxylates accelerate the reaction of lactones with oxiranes and aziridines.

Still another embodiment of the present invention is illustrated by the following equation:



where X is either O or N-R , and where R through R_8 can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and m is at least 1, representing at least one carbon in the lactone ring, and y is at least 1.

The following specific example illustrates one embodiment of this reaction:

Example 16. Reaction of gamma-butyrolactone with 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate.

Gamma butyrolactone, 3.2g (37.2 mmol) and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (commercially available as ERL 4221 from Union Carbide Corp.), 5.4g (21.4 mmol) were weighed into a 50 ml Erlenmeyer flask and thoroughly mixed. A portion, 2.2g, was transferred into a 25 ml Erlenmeyer flask for a control. To the remainder, 6.4g, was added 0.25g (0.3 % Cr based on the weight of the reactants) of the Cr^{+3} catalyst. The contents of both flasks were simultaneously heated to 97 to 100° C in a hot oil bath for a period of 3 hours. Samples were periodically taken over the 3 hour reaction period from the "control flask" for FTIR analysis.

Because the reactants containing the chromium catalyst polymerized into a resinous, rubbery solid mass after one hour of reaction, only one liquid sample could be taken 35 minutes after the reaction was started. While the absorption ratio of the ester peaks at 1773 cm^{-1} and 1729 cm^{-1} remained fairly constant, varying between 1.4:1.0 to 1.1:1.0, respectively, in the control run, the ratio in the only sample taken from the chromium catalyzed reaction before it polymerized into a solid mass was

4.6:1.0, showing the rapid formation of a new ester group. In contrast, the end of the three hour reaction time, the control sample was still liquid.

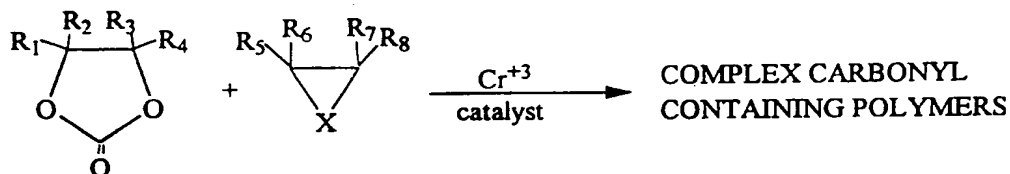
To see if the butyrolactone, alone, could be polymerized by the chromium catalyst, in a separate test, 4.0g of gamma butyrolactone was mixed with 0.5g of the Cr^{+3} catalyst (1.0 % of the butyrolactone weight) and heated to 99 °C for 4 hours. No polymerization occurred. The sample remained liquid.

All of these observations show that the Cr^{+3} catalyst accelerates the reaction and polymerization of gamma butyrolactone with 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate, without catalyzing homopolymerization of the gamma-butyrolactone.

It will be recognized by one of ordinary skill in the art that Example 16, above, and Examples 17 and 18, below, indicate that it appears that the Cr^{+3} carboxylate catalyst of the invention will accelerate the reaction between lactones and aziridines, as it accelerates the reaction between lactones and oxiranes. In such catalyzed reactions, the lactone, aziridine, and/or oxirane optionally can be polyfunctional.

2. Cr^{+3} carboxylate accelerates the reaction of carbonate esters with oxiranes and aziridines.

An alternative embodiment of the invention is illustrated by the following equation:



where X is either O and N-R , and where R through R_8 can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and the carbonate ester can be any molecular weight and composition, and the complex polymer that is formed represents, at a minimum, the reaction of one-mole of the three member ring with one-mole of the carbonate ester. The result of the reaction is a complex polymer.

One of ordinary skill in the art will readily recognize that each of the reactants of the catalyzed reaction can be either monofunctional or polyfunctional.

The following specific example illustrates one embodiment of this reaction:

Example 17. Reaction of propylene carbonate with 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate.

Propylene carbonate, 2.1g (20.4 mmol), and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (identified in Example 16, above), 2.8g (20.4 mmol), were weighed into a 50 ml Erlenmeyer flask and thoroughly mixed. A portion, 1.0g, was transferred into a 25 ml Erlenmeyer flask for a control. To the remainder, 3.9g, was added 0.2g (0.4% Cr based on the weight of the reactants) of the Cr^{+3} catalyst. The contents of both flasks were simultaneously heated to 75 to 94 °C in a hot oil bath for a period of 3 hours. Samples were periodically taken over the 3 hour reaction period from the "control flask" for FTIR analysis. Because the reactants containing the chromium catalyst polymerized into a resinous, rubbery solid mass after 40 minutes of reaction, only two liquid sample could be taken after the reaction was started. While the absorption ratio of the ester peaks at 1796 cm^{-1} and 1729 cm^{-1} remained constant at 1.2:1.0, respectively, in the control run, and was slightly higher (1.4-1.6:1.0, respectively) in the two samples taken from the chromium catalyzed reaction, at the end of the three hour reaction time, the control sample was still liquid at the end of the reaction.

To see if the propylene carbonate, alone, could be polymerized by the chromium catalyst, in a separate test, 2.3g of propylene carbonate was mixed with 0.25g of the Cr^{+3} catalyst (0.9% of the propylene carbonate weight) and heated to 98 °C for 3 hours and 20 minutes. No polymerization occurred. The sample remained liquid.

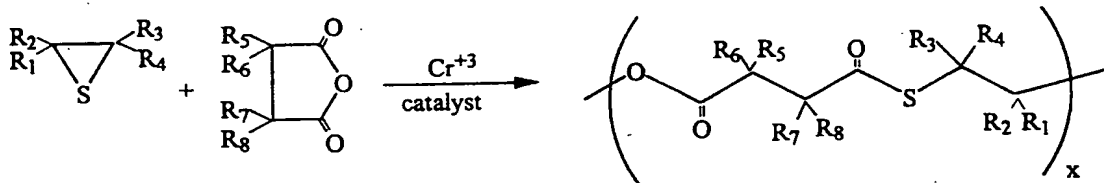
All of these observations show that the Cr^{+3} catalyst accelerates the reaction and polymerization of propylene carbonate with 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate.

Example 18. Reaction of propylene carbonate with pentaerythritol-tris-B-(N-aziridinyl)-propionate.

Into an aluminum weighing pan was put propylene carbonate, 2.2g (21.5 mmol), pentaerythritol-tris-B-(N-aziridinyl)-propionate (as identified in Example 1, above), 3.1g (7.3 mmol) and 1.0g of the Cr^{+3} catalyst (0.9 wt % chromium based on the weight of the reactants). The pan was allowed to stand at room temperature, 18°C, for 24 hours, during which time, the contents of the pan polymerized into a solid that was easily pulverized into a powder.

3. Cr^{+3} carboxylates accelerate the reaction of thiiranes with anhydrides.

Another embodiment of the present invention is illustrated by the following equation:



where R through R₈ can be made up of any combination of hydrogen, alkyl, alkene, alkyne, aryl, alkylaryl, cyano, azido, carboxy, oxo, hydroxy, halo or like kind substituted groups and x is at least 1. The result of the reaction will be the ring opening of thirane-rings with anhydrides.

In an alternative embodiment, one or more of the reactants of the reaction are polyfunctional.

The following specific example illustrates one embodiment of the present invention:

Example 19. Reaction of cyclohexene sulfide with methyl hexahydrophthalic anhydride (MHHPA).

Cyclohexene sulfide, 85 %, 3.3g (24.5 mmol) and MHHPA, 4.1g (24.4 mmol) were weighed into a 50 ml Erlenmeyer flask and thoroughly mixed. A small sample, 1.2 g was transferred into a 25 ml Erlenmeyer flask for a control. To the larger portion, 6.2 g, was added 0.8 g (1.0 % Cr based on the weight of the reactants) of the Cr⁺³ catalyst. The contents of both flasks were simultaneously heated to 98 to 102° C in a hot oil bath for a period of 3 hours and 15 minutes.

Samples were periodically taken from each flask for FTIR analysis. At the end of the reaction period the formation of two new carbonyl peaks (1729 cm⁻¹ and 1705 cm⁻¹) were seen to build up in the reaction flask containing the chromium catalyst but not in the control sample.

This example shows that Cr⁺³ will catalyze the reaction of a thirane (also known as epithiosulfides or ethylene sulfides) with an anhydride.

F. Further Evidence of the Unexpectedness of the Invention Results.

The embodiments of the Cr⁺³ invention catalyst detailed above represent unexpected results. The unexpectedness catalysis by the inventive catalyst is exemplified even further by the following specific examples which illustrate that Cr⁺³ carboxylate is not able to catalyze certain reactions:

1. The reaction of thiranes with carboxylic acids is not accelerated with Cr⁺³ carboxylate catalysts.

Example 20. Reaction of cyclohexene sulfide with 2-ethylhexanoic acid.

Cyclohexene sulfide, 85 %, 3.4g (25.3 mmol) and 2-ethylhexanoic acid, 3.5g (24.3 mmol) were weighed into a 50 ml Erlenmeyer flask and thoroughly mixed. A small sample, 1.2g was transferred into a 25 ml Erlenmeyer flask for a control. To the larger portion, 5.7g, was added 0.5g (0.7 % Cr based on the weight of the reactants) of the Cr^{+3} catalyst. The contents of both flasks were simultaneously heated to 98 to 102° C in a hot oil bath for a period of 3 hours and 25 minutes. Samples were periodically taken from each flask for FTIR analysis. At the end of the reaction period, no change in composition could be seen in either reaction flask.

2. The reaction of tetrahydrofurans with carboxylic acids is not accelerated with the Cr^{+3} carboxylate catalysts.

Example 21. Attempted reaction of 2-methyltetrahydrofuran with a dimer acid.

4.7g (7.8 mmol) of a dimer acid (as identified in Example 1, above), 1.5g (1.9 mmol) of 2-methyl-tetrahydrofuran, and 0.4g (0.5 % Cr based on the weight of the reactants) of the Cr^{+3} catalyst were weighed into a 50 ml Erlenmeyer flask and thoroughly mixed. The flask was heated to 60° C in a hot oil bath for a period of 1 1/3 hours. Samples were periodically taken for FTIR analysis. At the end of the reaction period, no new carbonyl or hydroxyl absorption was observed showing that the ring opening reaction of the 2-methyl-tetrahydrofuran did not occur.

INDUSTRIAL APPLICABILITY:

It is clear that the Cr^{+3} carboxylate catalysts of the invention will have wide applicability in industry to catalyze classes of reactions that heretofore have resisted effective catalytic processing. Further, the new classes of compounds produced by use of the Cr^{+3} carboxylate catalyst of the invention have properties of very evident interest. In addition, the new routes of synthesis that are made available by means of the catalyst open alternate processing schemes for the chemical industry.

It should be understood that various modifications within the scope of this invention can be made by one of ordinary skill in the art without departing from the spirit thereof. We therefore wish our invention to be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of the specification if need be.

We claim:

1. In a process for reacting at least one first component selected from:

- i) a heterocycle,
- ii) a monofunctional or polyfunctional thiirane,
- iii) a monofunctional or polyfunctional oxirane, and
- iv) a monofunctional or polyfunctional hydroxy compound,

with at least one second component selected from:

- i) a monofunctional or polyfunctional carbonyl-containing compound, and
- ii) a monofunctional or polyfunctional anhydride,

provided that where said first component is an oxirane, said second component is not a carboxylic acid, anhydride, or imide, and where said first component is a thiirane, said second component is not a carboxylic acid, to produce a reaction product, the improvement characterized by carrying out said reaction in the presence of a catalytically effective amount of C_3 - C_{60} , substituted or unsubstituted, straight or branch-chained, alkyl, aryl, or aralkyl carboxylate Cr^{+3} salt.

2. The process as in Claim 1, wherein said first component is a heterocycle selected from a monofunctional aziridine, a polyfunctional aziridine, a monofunctional oxetane, and a polyfunctional oxetane.

3. The process as in Claim 1 or Claim 2, wherein said second component is a carbonyl-containing compound selected from a lactone, a carbonate ester, a carboxylic acid, an anhydride, and an imide.

4. The process as in any one of Claims 1-3, wherein said Cr^{+3} carboxylate is selected from the group consisting of an octoate, an acetate, a butyrate, and a benzoate.

5. The process as in Claim 4, wherein said Cr^{+3} salt is a Cr^{+3} octoate.

6. The process as in Claim 5, wherein the Cr^{+3} concentration of the catalyst is from about 4 % to about 8 %.

7. The process as in any one of Claims 1-3, wherein the concentration of Cr^{+3} in the reaction media is from about 0.08% to about 2.0%, by weight, based on the combined weight of the reactants.
8. The process as in Claim 7, wherein the concentration of Cr^{+3} in the reaction media is from about 0.1% to about 0.7%, by weight, based on the combined weight of the reactants.
9. The process as in Claim 1 or Claim 3, wherein said anhydride is a copolymer of maleic anhydride and styrene.
10. The process as in Claim 9, wherein said hydroxy compound is a dihydroxy ester resin.
11. A product obtainable by reacting at least one first component selected from:
- i) a heterocycle,
 - ii) a monofunctional or polyfunctional thirane,
 - iii) a monofunctional or polyfunctional oxirane, and
 - iv) a monofunctional or polyfunctional hydroxy compound,
- with at least one second component selected from:
- i) a monofunctional or polyfunctional carbonyl-containing compound, and
 - ii) a monofunctional or polyfunctional anhydride,
- provided that where said first component is an oxirane, said second component is not a carboxylic acid, anhydride, or imide, and where said first component is a thirane, said second component is not a carboxylic acid, in the presence of a catalytically effective amount of $\text{C}_3\text{-C}_{60}$, substituted or unsubstituted, straight or branch-chained, alkyl, aryl, or aralkyl carboxylate Cr^{+3} salt.
12. The product as in Claim 11, wherein said first component is a heterocycle selected from a monofunctional aziridine, a polyfunctional aziridine, a monofunctional oxetane, and a polyfunctional oxetane.
13. The product as in Claim 11 or Claim 12, wherein said second component is a carbonyl-containing compound selected from a lactone, a carbonate ester, a carboxylic acid, an anhydride, and an imide.

14. The product as in any one of Claims 11-13, wherein said Cr^{+3} carboxylate is selected from the group consisting of an octoate, an acetate, a butyrate, and a benzoate.
15. The product as in Claim 14, wherein said Cr^{+3} salt is a Cr^{+3} octoate.
16. The product as in Claim 15, wherein the Cr^{+3} concentration of the catalyst is from about 4 % to about 8 %.
17. The product as in any one of Claims 11-13, wherein the concentration of Cr^{+3} in the reaction media is from about 0.08% to about 2.0%, by weight, based on the combined weight of the reactants.
18. The product as in Claim 17, wherein the concentration of Cr^{+3} in the reaction media is from about 0.1% to about 0.7%, by weight, based on the combined weight of the reactants.
19. The product as in Claim 11 or Claim 13, wherein said anhydride is a copolymer of maleic anhydride and styrene.
20. The product as in Claim 19, wherein said hydroxy compound is a dihydroxy ester resin.
21. A $\text{C}_3\text{-C}_{60}$, substituted or unsubstituted, straight or branch-chained, alkyl, aryl, or aralkyl carboxylate Cr^{+3} salt used as a catalyst for the reaction of at least one first component selected from:
- i) a heterocycle,
 - ii) a monofunctional or polyfunctional thiirane,
 - iii) a monofunctional or polyfunctional oxirane, and
 - iv) a monofunctional or polyfunctional hydroxy compound,
- with at least one second component selected from:
- i) a monofunctional or polyfunctional carbonyl-containing compound, and
 - ii) a monofunctional or polyfunctional anhydride,
- provided that where said first component is an oxirane, said second component is not a carboxylic acid, anhydride, or imide and where said first component is a thiirane, said second component is not a carboxylic acid.

22. The carboxylate Cr^{+3} salt as in Claim 21, wherein said first component is a heterocycle selected from a monofunctional aziridine, a polyfunctional aziridine, a monofunctional oxetane, and a polyfunctional oxetane.

23. The carboxylate Cr^{+3} salt as in Claim 21 or Claim 22, wherein said second component is a carbonyl-containing compound selected from a lactone, a carbonate ester, a carboxylic acid, an anhydride, and an imide.

24. The carboxylate Cr^{+3} salt as in any one of Claims 21-23, wherein said Cr^{+3} carboxylate is selected from the group consisting of an octoate, an acetate, a butyrate, and a benzoate.

25. The carboxylate Cr^{+3} salt as in Claim 24, wherein said Cr^{+3} salt is a Cr^{+3} octoate.

26. The carboxylate Cr^{+3} salt as in Claim 21 or 23, wherein said anhydride is a copolymer of maleic anhydride and styrene.

27. The carboxylate Cr^{+3} salt as in Claim 26, wherein said hydroxy compound is a dihydroxy ester resin.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/12251**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :Please See Extra Sheet.

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
HACHK'S CHEMICAL DICTIONARY

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS ONLINE

search terms: trivalent, chromium, catalys?, aziridin?, oxetane, thiirane, anhydrid?, carboxylat?, oxirane, imide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,635,869 A (STEELE et al) 18 January 1972, entire document.	1-3, 11-13, 21-23

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* "A" "B" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "G"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search

04 AUGUST 1998

Date of mailing of the international search report

29 SEP 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JANE C. OSWECKI

Telephone No. (703)308-1235

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/12251

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6: B01J 23/26, 31/34; C07C 53/124, 53/126, 53/134, 53/136, 57/145, 57/26, 59/01; C07D 207/404, 303/04, 305/04, 309/30, 331/02; C08K 5/01, 5/05, 5/09, 5/10, 5/3412, 5/45; C08L 63/00

A. CLASSIFICATION OF SUBJECT MATTER:

US CL: 523/456, 453, 455, 461; 502/170; 548/545, 969; 549/90, 263, 510, 512; 560/9, 19, 55, 76, 100, 103; 562/405, 426, 465, 490, 493, 887

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

523/456, 453, 455, 461; 502/170; 548/545, 969; 549/90, 263, 510, 512; 560/9, 19, 55, 76, 100, 103; 562/405, 426, 465, 490, 493, 887

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/12251

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-8, 9-10, 14-20, 24-27
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☐

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.